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EXHIBIT 9



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(54) **GOLF BALL CORES COMPRISING A HALOGENATED ORGANOSULFUR COMPOUND**

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(57) **ABSTRACT**

A golf ball formed of a core and a cover, wherein the core has a diameter of at least about 1.50 inches and comprises a polybutadiene rubber composition comprising at least about 2.2 parts per hundred of a halogenated organosulfur compound, and wherein the cover has a thickness of less than about 0.1 inches and comprises a polyurethane composition.

33 Claims, No Drawings

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GOLF BALL CORES COMPRISING A HALOGENATED ORGANOSULFUR COMPOUND

FIELD OF THE INVENTION

This invention relates generally to golf balls and, in particular, golf ball cores formed of a polymer composition including a halogenated organosulfur compound.

BACKGROUND

Conventional golf balls can be divided into two general classes: solid and wound. Solid golf balls include one-piece, two-piece (i.e., solid core and a cover), and multi-layer (i.e., solid core of one or more layers and/or a cover of one or more layers) golf balls. Wound golf balls typically include a solid, hollow, or fluid-filled center, surrounded by a tensioned elastomeric material, and a cover. Solid balls have traditionally been considered longer and more durable than wound balls, but also lack a particular "feel" provided by the wound construction.

By altering ball construction and composition, manufacturers can vary a wide range of playing characteristics, such as compression, velocity, and spin, each of which can be optimized for various playing abilities. One golf ball component, in particular, that many manufacturers are continually looking to improve is the center or core. The core becomes the "engine" of the golf ball when hit with a club head. Generally, golf ball cores and/or centers are constructed with a polybutadiene-based polymer composition. Compositions of this type are constantly being altered in an effort to provide a higher coefficient of restitution ("COR") while at the same time resulting in a lower compression which, in turn, can lower the golf ball spin rate, provide better "feel," or both. This is a difficult task, however, given the physical limitations of currently-available polymers. As such, there remains a need for novel and improved golf ball core compositions.

It has been determined that, upon that addition of a halogenated organosulfur compound or the salts thereof, in particular, pentachlorothiophenol ("PCTP") salt, to polybutadiene rubber compositions, that golf ball cores may be constructed that exhibit increased COR, decreased compression, or both. The present invention is, therefore, directed to golf ball centers and cores that include a halogenated organosulfur compound, or a salt thereof, for embodiments such as these.

SUMMARY OF THE INVENTION

The present invention is directed to a golf ball formed of a core and a cover, wherein the core has a diameter of at least about 1.50 inches and comprises a polybutadiene rubber composition comprising at least about 2.2 parts per hundred of a halogenated organosulfur compound, and wherein the cover has a thickness of less than about 0.1 inches and comprises a polyurethane composition.

The core can include a center and an outer core layer and the core preferably has a diameter of at least about 1.55 inches. The cover may include an inner cover layer and an outer cover layer and, preferably, at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches. The inner cover layer may include an ionomeric material, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

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rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

The polybutadiene rubber composition may include between about 2.2 parts and about 5 parts of a halogenated organosulfur compound. The halogenated organosulfur compound may include pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof, and mixtures thereof, but is preferably pentachlorothiophenol or the metal salt thereof. The metal salt may be zinc, calcium, potassium, magnesium, sodium, and lithium, but is preferably zinc.

In one embodiment, the core has a compression less than about 75 and the golf ball has a coefficient of restitution of greater than about 0.800. In another, the core has a compression less than about 75 and the golf ball has a coefficient of restitution of greater than about 0.815. In still another, the core has a compression less than about 55 and the golf ball has a coefficient of restitution of greater than about 0.800.

The polybutadiene composition may further include an α,β -unsaturated carboxylic acid or a metal salt thereof, an organic peroxide, and a filler. If the outer cover layer includes polyurethane, it includes a prepolymer formed of a polyisocyanate and a polyol, and a curing agent. Preferably, at least one of the prepolymer and curing agent are saturated. In an alternative embodiment, the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

The present invention is also directed to a golf ball formed of a core and a cover, wherein the core has a diameter of at least about 1.50 inches and comprises a polybutadiene rubber composition comprising at least about 2.2 parts per hundred of a halogenated organosulfur compound, and wherein the cover has a thickness of less than about 0.1 inches and is formed of an inner cover layer and an outer cover layer.

In one embodiment, the core comprises a center having an outer diameter of at least about 1.55 inches and an outer core layer. It is preferred that at least one of the inner and outer cover layers have a thickness of less than about 0.05 inches. Either of the cover layers may include vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, partially-neutralized polymers, and mixtures thereof.

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The polybutadiene rubber composition preferably includes between about 2.2 parts and about 5 parts of a halogenated organosulfur compound. The halogenated organosulfur compound can be pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromo thiophenol; 3-bromo thiophenol; 4-bromo thiophenol; 2,3-bromo thiophenol; 2,4-bromo thiophenol; 3,4-bromo thiophenol; 3,5-bromo thiophenol; 2,3,4-bromo thiophenol; 3,4,5-bromo thiophenol; 2,3,4,5-tetrabromo thiophenol; 2,3,5,6-tetrabromo thiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof, and mixtures thereof, and preferably is pentachlorothiophenol or the metal salt thereof. The metal salt is selected from the group consisting of zinc, calcium, potassium, magnesium, sodium, and lithium and is preferably zinc.

The core compression is preferably less than about 75 and the golf ball coefficient of restitution preferably greater than about 0.800. In one embodiment, the core has a compression less than about 75 and the golf ball has a coefficient of restitution of greater than about 0.815. In another, the core has a compression less than about 55 and the golf ball has a coefficient of restitution of greater than about 0.800. In still another, the polybutadiene composition further comprises an α,β -unsaturated carboxylic acid or a metal salt thereof, an organic peroxide, and a filler.

In another embodiment, the outer cover layer is formed of a polyurethane composition comprising a prepolymer formed of a polyisocyanate and a polyol, and a curing agent. At least one of the prepolymer and curing agent are saturated. In a preferred embodiment, the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

The present invention is also directed to a golf ball formed of a core and a cover, wherein the core has a diameter of at least about 1.55 inches and comprises a polybutadiene rubber composition comprising greater than about 2.3 parts per hundred of pentachlorothiophenol or a metal salt thereof, and wherein the cover comprises an inner cover layer comprising an ionomeric material and having a thickness of less than about 0.04 inches; and an outer cover layer having a thickness of less than about 0.04 inches and comprising a polyurethane composition.

DETAILED DESCRIPTION

The golf ball cores of the present invention may comprise any of a variety of constructions but preferably includes a core and a cover surrounding the core. The core and/or the cover may have more than one layer and an intermediate layer may be disposed between the core and the cover of the

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golf ball. For example, the core of the golf ball may comprise a conventional center surrounded by an intermediate or outer core layer disposed between the center and the inner cover layer. The core may be a single layer or may comprise a plurality of layers. The innermost portion of the core may be solid or it may be a liquid filled sphere, but preferably it is solid. As with the core, the intermediate layer or outer core layer may also comprise a plurality of layers. The core may also comprise a solid or liquid filled center around which many yards of a tensioned elastomeric material are wound.

The materials for solid cores include compositions having a base rubber, a crosslinking agent, a filler, a halogenated organosulfur compound, and a co-crosslinking or initiator agent. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at least 40%, more preferably at least about 90%, and most preferably at least about 95%. Most preferably, the base rubber comprises high-Mooney-viscosity rubber. Preferably, the base rubber has a Mooney viscosity greater than about 35, more preferably greater than about 50. Preferably, the polybutadiene rubber has a molecular weight greater than about 400,000 and a polydispersity of no greater than about 2. Examples of good desirable polybutadiene rubbers include BUNA® CB22 and BUNA® CB23, commercially available from Bayer of Akron, Ohio; UBEPOL® 360L and UBEPOL® 150L, commercially available from UBE Industries of Tokyo, Japan; and CARIFLEX® BCP820 and CARIFLEX® BCP824, commercially available from Shell of Houston, Tex. If desired, the polybutadiene can also be mixed with other elastomers known in the art such as natural rubber, polyisoprene rubber and/or styrene-butadiene rubber in order to modify the properties of the core.

The crosslinking agent includes a metal salt, such as a zinc salt or a magnesium unsaturated fatty acid, having 3 to 8 carbon atoms. Examples include, but are not limited to, one or more metal salt diacrylates, dimethacrylates, and monomethacrylates, wherein the metal is magnesium, calcium, zinc, aluminum, sodium, lithium, or nickel. Preferred acrylates include zinc acrylate, zinc diacrylate, zinc methacrylate, zinc dimethacrylate, and mixtures thereof. The crosslinking agent is typically present in an amount greater than about 10 parts per hundred ("pph") parts of the base polymer, preferably from about 20 to 40 pph of the base polymer, more preferably from about 25 to 35 pph of the base polymer.

The initiator agent can be any known polymerization initiator which decomposes during the cure cycle. Suitable initiators include organic peroxide compounds, such as dicumyl peroxide; 1,1-di(t-butylperoxy) 3,3,5-trimethyl cyclohexane; α,α -bis (t-butylperoxy) diisopropylbenzene; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; di-t-butyl peroxide; and mixtures thereof. Other examples include, but are not limited to, VAROX® 231XL and Varox® DCP-R, commercially available from Elf Atochem of Philadelphia, Pa.; PERKODOX® BC and PERKODOX® 14, commercially available from Akzo Nobel of Chicago, Ill.; and ELASTOCHEM® DCP-70, commercially available from Rhein Chemie of Trenton, N.J.

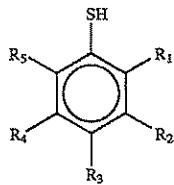
It is well known that peroxides are available in a variety of forms having different activity. The activity is typically defined by the "active oxygen content." For example, PERKODOX® BC peroxide is 98% active and has an active oxygen content of 5.80%, whereas PERKODOX® DCP-70 is 70% active and has an active oxygen content of 4.18%. If the peroxide is present in pure form, it is preferably present

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in an amount of at least about 0.25 pph, more preferably between about 0.35 pph and about 2.5 pph, and most preferably between about 0.5 pph and about 2 pph. Peroxides are also available in concentrate form, which are well-known to have differing activities, as described above. In this case, if concentrate peroxides are employed in the present invention, one skilled in the art would know that the concentrations suitable for pure peroxides are easily adjusted for concentrate peroxides by dividing by the activity. For example, 2 pph of a pure peroxide is equivalent 4 pph of a concentrate peroxide that is 50% active (i.e., 2 divided by 0.5=4).

The halogenated organosulfur compounds of the present invention include, but are not limited to those having the following general formula:



where R₁-R₅ can be C₁-C₈ alkyl groups; halogen groups; thiol groups (-SH), carboxylated groups; sulfonated groups; and hydrogen; in any order; and also pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts. Preferably, the halogenated organosulfur compound is pentachlorothiophenol, which is commercially available in neat form or under the tradename STRUKTOL®, a clay-based carrier containing the sulfur compound pentachlorothiophenol loaded at 45 percent (correlating to 2.4 parts PCIP). STRUKTOL® is commercially available from Struktol Company of America of Stow, Ohio. PCIP is commercially available in neat form from eChinachem of San Francisco, Calif. and in the salt form from eChinachem of San Francisco, Calif. Most preferably, the halogenated organosulfur compound is the zinc salt of pentachlorothiophenol, which is commercially available from eChinachem of San Francisco, Calif. The halogenated organosulfur compounds of the present invention are preferably present in an amount greater than about 2.2 pph, more preferably between about 2.3 pph and about 5 pph, and most preferably between about 2.3 and about 4 pph.

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Fillers typically include materials such as tungsten, zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate, metals, metal oxides and salts, regrind (recycled core material typically ground to about 30 mesh particle), high-Mooney-viscosity rubber regrind, and the like. Fillers added to one or more portions of the golf ball typically include processing aids or compounds to affect rheological and mixing properties, density-modifying fillers, tear strength, or reinforcement fillers, and the like. The fillers are generally inorganic, and suitable fillers include numerous metals or metal oxides, such as zinc oxide and tin oxide, as well as barium sulfate, zinc sulfate, calcium carbonate, barium carbonate, clay, tungsten, tungsten carbide, an array of silicas, and mixtures thereof. Fillers may also include various foaming agents or blowing agents which may be readily selected by one of ordinary skill in the art. Fillers may include polymeric, ceramic, metal, and glass microspheres may be solid or hollow, and filled or unfilled. Fillers are typically also added to one or more portions of the golf ball to modify the density thereof to conform to uniform golf ball standards. Fillers may also be used to modify the weight of the center or at least one additional layer for specialty balls, e.g., a lower weight ball is preferred for a player having a low swing speed.

25 The invention also includes a method to convert the cis-isomer of the polybutadiene resilient polymer component to the trans-isomer during a molding cycle and to form a golf ball. A variety of methods and materials suitable for cis-to-trans conversion have been disclosed in U.S. Pat. No. 6,162,135 and U.S. application Ser. Nos. 09/461,736, filed Dec. 16, 1999; 09/458,676, filed Dec. 10, 1999; and 09/461,421, filed Dec. 16, 1999, each of which are incorporated herein, in their entirety, by reference.

30 The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a mixture by any type of mixing known to one of ordinary skill in the art. Suitable types of mixing include single pass and multi-pass mixing. Suitable mixing equipment is well known to those of ordinary skill in the art, and such equipment may include a Banbury mixer, a two-roll mill, or a twin screw extruder.

35 Conventional mixing speeds for combining polymers are typically used. The mixing temperature depends upon the type of polymer components, and more importantly, on the type of free-radical initiator. Suitable mixing speeds and temperatures are well-known to those of ordinary skill in the art, or may be readily determined without undue experimentation.

40 The mixture can be subjected to, e.g., a compression or injection molding process, to obtain solid spheres for the center or hemispherical shells for forming an intermediate layer. The temperature and duration of the molding cycle are selected based upon reactivity of the mixture. The molding cycle may have a single step of molding the mixture at a single temperature for a fixed time duration. The molding cycle may also include a two-step process, in which the polymer mixture is held in the mold at an initial temperature for an initial duration of time, followed by holding at a second, typically higher temperature for a second duration of time. In a preferred embodiment of the current invention, a single-step cure cycle is employed. The materials used in forming either the golf ball center or any portion of the core, in accordance with the invention, may be combined to form a golf ball by an injection molding process, which is also well-known to one of ordinary skill in the art. Although the curing time depends on the various materials selected, those of ordinary skill in the art will be readily able to adjust the

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curing time upward or downward based on the particular materials used and the discussion herein.

Properties that are desirable for the cover include good moldability, high abrasion resistance, high tear strength, high resilience, and good mold release. The cover typically has a thickness to provide sufficient strength, good performance characteristics, and durability. The cover preferably has a thickness of less than about 0.1 inches, more preferably, less than about 0.05 inches, and most preferably, between about 0.02 inches and about 0.04 inches. The invention is particularly directed towards a multilayer golf ball which comprises a core, an inner cover layer, and an outer cover layer. In this embodiment, preferably, at least one of the inner and outer cover layer has a thickness of less than about 0.05 inches, more preferably between about 0.02 inches and about 0.04 inches. Most preferably, the thickness of either layer is about 0.03 inches.

When the golf ball of the present invention includes an inner cover layer, this layer can include any materials known to those of ordinary skill in the art, including thermoplastic and thermosetting material, but preferably the inner cover can include any suitable materials, such as ionic copolymers of ethylene and an unsaturated monocarboxylic acid which are available under the trademark SURLYN of E.I. DuPont de Nemours & Co., of Wilmington, Del., or IOTEK or ESCOR of Exxon. These are copolymers or terpolymers of ethylene and methacrylic acid or acrylic acid partially neutralized with salts of zinc, sodium, lithium, magnesium, potassium, calcium, manganese, nickel or the like, in which the salts are the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially neutralized and might include methacrylic, crotonic, maleic, fumaric or itaconic acid.

This golf ball can likewise include one or more homopolymeric or copolymeric inner cover materials, such as:

- (1) Vinyl resins, such as those formed by the polymerization of vinyl chloride, or by the copolymerization of vinyl chloride with vinyl acetate, acrylic esters or vinylidene chloride;
- (2) Polyolefins, such as polyethylene, polypropylene, polybutylene and copolymers such as ethylene methylacrylate, ethylene ethylacrylate, ethylene vinyl acetate, ethylene methacrylic or ethylene acrylic acid or propylene acrylic acid and copolymers and homopolymers produced using a single-site catalyst or a metallocene catalyst;
- (3) Polyurethanes, such as those prepared from polyols and diisocyanates or polyisocyanates and those disclosed in U.S. Pat. No. 5,334,673;
- (4) Polyureas, such as those disclosed in U.S. Pat. No. 5,484,870;
- (5) Polyamides, such as poly(hexamethylene adipamide) and others prepared from diamines and dibasic acids, as well as those from amino acids such as poly (caprolactam), and blends of polyamides with SURLYN, polyethylene, ethylene copolymers, ethylene-propylene-non-conjugated diene terpolymer, and the like;
- (6) Acrylic resins and blends of these resins with polyvinyl chloride, elastomers, and the like;
- (7) Thermoplastics, such as urethanes; olefinic thermoplastic rubbers, such as blends of polyolefins with ethylene-propylene-non-conjugated diene terpolymer;

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block copolymers of styrene and butadiene, isoprene or ethylene-butylene rubber; or copoly(ether-amide), such as PEBAK, sold by ELF Atochem of Philadelphia, Pa.;

(8) Polyphenylene oxide resins or blends of polyphenylene oxide with high impact polystyrene as sold under the trademark NORYL by General Electric Company of Pittsfield, Mass.;

(9) Thermoplastic polyesters, such as polyethylene terephthalate, polybutylene terephthalate, polyethylene terephthalate/glycol modified and elastomers sold under the trademarks HYTREL by E.I. DuPont de Nemours & Co. of Wilmington, Del., and LOMOD by General Electric Company of Pittsfield, Mass.;

(10) Blends and alloys, including polycarbonate with acrylonitrile butadiene styrene, polybutylene terephthalate, polyethylene terephthalate, styrene maleic anhydride, polyethylene, elastomers, and the like, and polyvinyl chloride with acrylonitrile butadiene styrene or ethylene vinyl acetate or other elastomers; and

(11) Blends of thermoplastic rubbers with polyethylene, propylene, polyacetal, nylon, polyesters, cellulose esters, and the like.

Preferably, the inner cover includes polymers, such as ethylene, propylene, butene-1 or hexane-1 based homopolymers or copolymers including functional monomers, such as acrylic and methacrylic acid and fully or partially neutralized ionomer resins and their blends, methyl acrylate, methyl methacrylate homopolymers and copolymers, imidized, amino group containing polymers, polycarbonate, reinforced polyamides, polyphenylene oxide, high impact polystyrene, polyether ketone, polysulfone, poly(phenylene sulfide), acrylonitrile-butadiene, acrylic-styrene-acrylonitrile, poly(ethylene terephthalate), poly(butylene terephthalate), poly(ethelyne vinyl alcohol), poly(tetrafluoroethylene) and their copolymers including functional comonomers, and blends thereof. Suitable cover compositions also include a polyether or polyester thermoplastic urethane, a thermoset polyurethane, a low modulus ionomer, such as acid-containing ethylene copolymer ionomers, including E/X/Y terpolymers where E is ethylene, X is an acrylate or methacrylate-based softening comonomer present in about 0 to 50 weight percent and Y is acrylic or methacrylic acid present in about 5 to 35 weight percent. Preferably, the acrylic or methacrylic acid is present in about 8 to 35 weight percent, more preferably 8 to 25 weight percent, and most preferably 8 to 20 weight percent.

Any of the inner or outer cover layers may also be formed from polymers containing α,β -unsaturated carboxylic acid groups, or the salts thereof, that have been 100 percent neutralized by organic fatty acids. The acid moieties of the highly-neutralized polymers ("HNP"), typically ethylene-based ionomers, are preferably neutralized greater than about 70%, more preferably greater than about 90%, and most preferably at least about 100%. The HNP's can be also be blended with a second polymer component, which, if containing an acid group, may be neutralized in a conventional manner, by the organic fatty acids of the present invention, or both. The second polymer component, which may be partially or fully neutralized, preferably comprises ionomeric copolymers and terpolymers, ionomer precursors, thermoplastics, polyamides, polycarbonates, polyesters, polyurethanes, polyureas, thermoplastic elastomers, polybutadiene rubber, balata, metallocene-catalyzed polymers (grafted and non-grafted), single-site polymers, high-crystalline acid polymers, cationic ionomers, and the like.

The acid copolymers can be described as E/X/Y copolymers where E is ethylene, X is an α,β -ethylenically unsat-

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urated carboxylic acid, and Y is a softening comonomer. In a preferred embodiment, X is acrylic or methacrylic acid and Y is a C₁₋₈ alkyl acrylate or methacrylate ester. X is preferably present in an amount from about 1 to about 35 weight percent of the polymer, more preferably from about 5 to about 30 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer. Y is preferably present in an amount from about 0 to about 50 weight percent of the polymer, more preferably from about 5 to about 25 weight percent of the polymer, and most preferably from about 10 to about 20 weight percent of the polymer.

The organic acids are aliphatic, mono-functional (saturated, unsaturated, or multi-unsaturated) organic acids. Salts of these organic acids may also be employed. The salts of organic acids of the present invention include the salts of barium, lithium, sodium, zinc, bismuth, chromium, cobalt, copper, potassium, strontium, titanium, tungsten, magnesium, cesium, iron, nickel, silver, aluminum, tin, or calcium, salts of fatty acids, particularly stearic, behenic, erucic, oleic, linoleic or dimerized derivatives thereof. It is preferred that the organic acids and salts of the present invention be relatively non-migratory (they do not bloom to the surface of the polymer under ambient temperatures) and non-volatile (they do not volatilize at temperatures required for melt-blending).

Thermoplastic polymer components, such as copolyetheresters, copolyesteresters, copolyetheramides, elastomeric polyolefins, styrene diene block copolymers and their hydrogenated derivatives, copolyesteramides, thermoplastic polyurethanes, such as copolyetherurethanes, copolyesterurethanes, copolyureaurethanes, epoxy-based polyurethanes, polycaprolactone-based polyurethanes, polyureas, and polycarbonate-based polyurethanes fillers, and other ingredients, if included, can be blended in either before, during, or after the acid moieties are neutralized, thermoplastic polyurethanes.

Examples of these materials are disclosed in U.S. patent application Publication Nos. 2001/0018375 and 2001/0019971, which are incorporated herein in their entirety by express reference thereto.

While the outer cover may be formed of any of the above-listed materials, the outer cover preferably includes a polyurethane, polyurea, or epoxy composition, generally comprising the reaction product of at least one polyisocyanate, polyol, and at least one curing agent. Any polyisocyanate available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyisocyanates include, but are not limited to, 4,4'-diphenylmethane diisocyanate ("MDI"); polymeric MDI; carbodiimide-modified liquid MDI; 4,4'-dicyclohexylmethane diisocyanate ("H₁₂MDI"); p-phenylene diisocyanate ("PPDI"); m-phenylene diisocyanate ("MPDI"); toluene diisocyanate ("TDI"); 3,3'-dimethyl-4,4'-biphenylene diisocyanate ("TODI"); isophorone diisocyanate ("IPDI"); hexamethylene diisocyanate ("HDI"); naphthalene diisocyanate ("NDI"); xylene diisocyanate ("XDI"); p-tetramethylxylene diisocyanate ("p-TMXDI"); m-tetramethylxylene diisocyanate ("m-TMXDI"); ethylene diisocyanate; propylene 1,2-diisocyanate; tetramethylene 1,4-diisocyanate; cyclohexyl diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); dodecane-1,12-diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,4,4-

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trimethyl-1,6-hexane diisocyanate ("TMDI"); tetracene diisocyanate; naphthalene diisocyanate; anthracene diisocyanate; isocyanurate of toluene diisocyanate; uretdione of hexamethylene diisocyanate; and mixtures thereof. Preferably, the polyisocyanate includes MDI, PPDI, TDI, or a mixture thereof, and more preferably, the polyisocyanate includes MDI. It should be understood that, as used herein, the term "MDI" includes 4,4'-diphenylmethane diisocyanate, polymeric MDI, carbodiimide-modified liquid MDI, and mixtures thereof and, additionally, that the diisocyanate employed may be "low free monomer," understood by one of ordinary skill in the art to have lower levels of "free" monomer isocyanate groups, typically less than about 0.1% free monomer groups. Examples of "low free monomer" diisocyanates include, but are not limited to Low Free Monomer MDI, Low Free Monomer TDI, and Low Free Monomer PPDI.

The at least one polyisocyanate should have less than about 14% unreacted NCO groups. Preferably, the at least one polyisocyanate has no greater than about 7.5% NCO, and more preferably, less than about 7.0%.

Any polyol available to one of ordinary skill in the art is suitable for use according to the invention. Exemplary polyols include, but are not limited to, polyether polyols, hydroxy-terminated polybutadiene (including partially/fully hydrogenated derivatives), polyester polyols, polycaprolactone polyols, and polycarbonate polyols. In one preferred embodiment, the polyol includes polyether polyol. Examples include, but are not limited to, polytetramethylene ether glycol ("PTMEG"), polyethylene propylene glycol, polyoxypolypropylene glycol, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds and substituted or unsubstituted aromatic and cyclic groups. Preferably, the polyol of the present invention includes PTMEG.

Suitable polyester polyols include, but are not limited to, polyethylene adipate glycol; polybutylene adipate glycol; polyethylene propylene adipate glycol; o-phthalate-1,6-hexanediol; poly(hexamethylene adipate) glycol; and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycaprolactone polyols include, but are not limited to, 1,6-hexanediol-initiated polycaprolactone, diethylene glycol initiated polycaprolactone, trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, 1,4-butanediol-initiated polycaprolactone, PTMEG-initiated polycaprolactone, and mixtures thereof. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Suitable polycarbonates include, but are not limited to, polyphthalate carbonate and poly(hexamethylene carbonate) glycol. The hydrocarbon chain can have saturated or unsaturated bonds, or substituted or unsubstituted aromatic and cyclic groups.

Polyamine curatives are also suitable for use in polyurethane covers. Preferred polyamine curatives include, but are not limited to, 3,5-dimethylthio-2,4-toluenediamine and isomers thereof; 3,5-diethyltoluene-2,4-diamine and isomers thereof, such as 3,5-diethyltoluene-2,6-diamine; 4,4'-bis-(sec-butylamino)-diphenylmethane; 1,4-bis-(sec-butylamino)-benzene, 4,4'-methylene-bis-(2-chloroaniline); 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline) ("MCDEA"); polytetramethyleneoxide-di-p-aminobenzoate; N,N-dialkylamino diphenyl methane; p,p'-methylene dianiline ("MDA"); m-phenylenediamine

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("MPDA"); 4,4'-methylene-bis-(2-chloroaniline) ("MOCA"); 4,4'-methylene-bis-(2,6-diethylaniline) ("MDEA"); 4,4'-methylene-bis-(2,3-dichloroaniline) ("MDCA"); 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl diphenylmethane; 2,2',3,3'-tetrachloro diamino diphenylmethane; trimethylene glycol di-p-aminobenzoate; and mixtures thereof. Preferably, the curing agent of the present invention includes 3,5-dimethylthio-2,4-toluenediamine and isomers thereof, such as Ethacure® 300, commercially available from Albermarle Corporation of Baton Rouge, La. Suitable polyamine curatives include both primary and secondary amines.

At least one of a diol, triol, tetraol, or hydroxy-terminated curatives may be added to the aforementioned polyurethane composition. Suitable diol, triol, and tetraol groups include ethylene glycol; diethylene glycol; polyethylene glycol; propylene glycol; polypropylene glycol; lower molecular weight polytetramethylene ether glycol; 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,4-butanediol; 1,5-pantanediol; 1,6-hexanediol; resorcinol-di-(β-hydroxyethyl) ether; hydroquinone-di-(β-hydroxyethyl) ether; and mixtures thereof. Preferred hydroxy-terminated curatives include 1,3-bis(2-hydroxyethoxy) benzene; 1,3-bis-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,3-bis-[2-[2-(2-hydroxyethoxy) ethoxy] benzene; 1,4-butanediol, and mixtures thereof.

Both the hydroxy-terminated and amine curatives can include one or more saturated, unsaturated, aromatic, and cyclic groups. Additionally, the hydroxy-terminated and amine curatives can include one or more halogen groups. The polyurethane composition can be formed with a blend or mixture of curing agents. If desired, however, the polyurethane composition may be formed with a single curing agent.

In a particularly preferred embodiment of the present invention, saturated polyurethanes used to form cover layers, preferably the outer cover layer, and may be selected from among both castable thermoset and thermoplastic polyurethanes. In this embodiment, the saturated polyurethanes are substantially free of aromatic groups or moieties.

Saturated diisocyanates which can be used include, but are not limited to, ethylene diisocyanate; propylene-1,2-diisocyanate; tetramethylene-1,4-diisocyanate; 1,6-hexamethylene-diisocyanate ("HDI"); 2,2,4-trimethylhexamethylene diisocyanate; 2,4,4-trimethylhexamethylene diisocyanate; dodecane-1,12-diisocyanate; dicyclohexylmethane diisocyanate; cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane; isophorone diisocyanate ("IPDI"); methyl cyclohexylene diisocyanate; triisocyanate of HDI; triisocyanate of 2,2,4-trimethyl-1,6-hexane diisocyanate ("TMDI"). The most preferred saturated diisocyanates are 4,4'-dicyclohexylmethane diisocyanate ("HMDI") and isophorone diisocyanate ("IPDI").

Saturated polyols which are appropriate for use in this invention include, but are not limited to, polyether polyols such as polytetramethylene ether glycol and poly(oxypropylene) glycol. Suitable saturated polyester polyols include polyethylene adipate glycol, polyethylene propylene adipate glycol, polybutylene adipate glycol, polycarbonate polyol and ethylene oxide-capped polyoxypropylene diols. Saturated polycaprolactone polyols which are useful in the invention include diethylene glycol initiated

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polycaprolactone, 1,4-butanediol initiated polycaprolactone, 1,6-hexanediol initiated polycaprolactone; trimethylol propane initiated polycaprolactone, neopentyl glycol initiated polycaprolactone, PTMEG-initiated polycaprolactone. The most preferred saturated polyols are PTMEG and PTMEG-initiated polycaprolactone.

Suitable saturated curatives include 1,4-butanediol, ethylene glycol, diethylene glycol, polytetramethylene ether glycol, propylene glycol; trimethanolpropane; tetra-(2-hydroxypropyl)-ethylenediamine; isomers and mixtures of isomers of cyclohexylidemethylol, isomers and mixtures of isomers of cyclohexane bis(methylamine); triisopropanolamine, ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, 4,4'-dicyclohexylmethane diamine, 2,2,4-trimethyl-1,6-hexanediamine; 2,4,4-trimethyl-1,6-hexanediamine; diethyleneglycol di-(aminopropyl)ether; 4,4'-bis-(sec-butylamino)-dicyclohexylmethane; 1,2-bis-(sec-butylamino)cyclohexane; 1,4-bis-(sec-butylamino)cyclohexane; isophorone diamine, hexamethylene diamine, propylene diamine, 1-methyl-2,4-cyclohexyl diamine, 1-methyl-2,6-cyclohexyl diamine, 1,3-diaminopropane, dimethylamino propylamine, diethylamino propylamine, imido-bis-propylamine, isomers and mixtures of isomers of diaminocyclohexane, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, and diisopropanolamine. The most preferred saturated curatives are 1,4-butanediol, 1,4-cyclohexylidemethylol and 4,4'-bis-(sec-butylamino)-dicyclohexylmethane.

Suitable catalysts include, but are not limited to bismuth catalyst, oleic acid, triethylenediamine (DABCO®-33LV), di-butyltin dilaurate (DABCO®-T12) and acetic acid. The most preferred catalyst is di-butyltin dilaurate (DABCO®-T12). DABCO® materials are manufactured by Air Products and Chemicals, Inc.

It is well known in the art that if the saturated polyurethane materials are to be blended with other thermoplastics, care must be taken in the formulation process so as to produce an end product which is thermoplastic in nature. Thermoplastic materials may be blended with other thermoplastic materials, but thermosetting materials are difficult if not impossible to blend homogeneously after the thermosetting materials are formed. Preferably, the saturated polyurethane comprises from about 1 to about 100%, more preferably from about 10 to about 75% of the cover composition and/or the intermediate layer composition. About 90 to about 10%, more preferably from about 90 to about 25% of the cover and/or the intermediate layer composition is comprised of one or more other polymers and/or other materials as described below. Such polymers include, but are not limited to polyurethane/polyurea ionomers, polyurethanes or polyureas, epoxy resins, polyethylenes, polyamides and polyesters, polycarbonates and polyacrylin. Unless otherwise stated herein, all percentages are given in percent by weight of the total composition of the golf ball layer in question.

Polyurethane prepolymers are produced by combining at least one polyol, such as a polyether, polycaprolactone, polycarbonate or a polyester, and at least one isocyanate. Thermosetting polyurethanes are obtained by curing at least one polyurethane prepolymer with a curing agent selected from a polyamine, triol or tetraol. Thermoplastic polyurethanes are obtained by curing at least one polyurethane prepolymer with a diol curing agent. The choice of the curatives is critical because some urethane elastomers that are cured with a diol and/or blends of diols do not produce urethane elastomers with the impact resistance required in a

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golf ball cover. Blending the polyamine curatives with diol cured urethane elastomeric formulations leads to the production of thermoset urethanes with improved impact and cut resistance.

Thermoplastic polyurethanes may be blended with suitable materials to produce a thermoplastic end product. Examples of such additional materials may include ionomers such as the SURLYN®, ESCOR® and IOTEK® copolymers described above.

Other suitable materials which may be combined with the saturated polyurethanes in forming the cover and/or intermediate layer(s) of the golf balls of the invention include ionic or non-ionic polyurethanes and polyureas, epoxy resins, polyethylenes, polyamides and polyesters. For example, the cover and/or intermediate layer may be formed from a blend of at least one saturated polyurethane and thermoplastic or thermoset ionic and non-ionic urethanes and polyurethanes, cationic urethane ionomers and urethane epoxies, ionic and non-ionic polyureas and blends thereof. Examples of suitable urethane ionomers are disclosed in U.S. Pat. No. 5,692,974 entitled "Golf Ball Covers," the disclosure of which is hereby incorporated by reference in its entirety. Other examples of suitable polyurethanes are described in U.S. Pat. No. 5,334,673. Examples of appropriate polyureas are discussed in U.S. Pat. No. 5,484,870 and examples of suitable polyurethanes cured with epoxy group containing curing agents are disclosed in U.S. Pat. No. 5,908,358, the disclosures of which are hereby incorporated herein by reference in their entirety.

A variety of conventional components can be added to the cover compositions of the present invention. These include, but are not limited to, white pigment such as TiO₂, ZnO, optical brighteners, surfactants, processing aids, foaming agents, density-controlling fillers, UV stabilizers and light stabilizers. Saturated polyurethanes are resistant to discoloration. However, they are not immune to deterioration in their mechanical properties upon weathering. Addition of UV absorbers and light stabilizers to any of the above compositions and, in particular, the polyurethane compositions, help to maintain the tensile strength, elongation, and color stability. Suitable UV absorbers and light stabilizers include TINUVIN® 328, TINUVIN® 213, TINUVIN® 765, TINUVIN® 770 and TINUVIN® 622. The preferred UV absorber is TINUVIN® 328, and the preferred light stabilizer is TINUVIN® 765. TINUVIN® products are available from Ciba-Geigy. Dyes, as well as optical brighteners and fluorescent pigments may also be included in the golf ball covers produced with polymers formed according to the present invention. Such additional ingredients may be added in any amounts that will achieve their desired purpose.

Any method known to one of ordinary skill in the art may be used to polyurethanes of the present invention. One commonly employed method, known in the art as a one-shot method, involves concurrent mixing of the polyisocyanate, polyol, and curing agent. This method results in a mixture that is inhomogenous (more random) and affords the manufacturer less control over the molecular structure of the resultant composition. A preferred method of mixing is known as a prepolymer method. In this method, the polyisocyanate and the polyol are mixed separately prior to addition of the curing agent. This method affords a more homogeneous mixture resulting in a more consistent polymer composition. Other methods suitable for forming the layers of the present invention include reaction injection molding ("RIM"), liquid injection molding ("LIM"), and pre-reacting the components to form an injection moldable

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thermoplastic polyurethane and then injection molding, all of which are known to one of ordinary skill in the art.

It has been found by the present invention that the use of a castable, reactive material, which is applied in a fluid form, makes it possible to obtain very thin outer cover layers on golf balls. Specifically, it has been found that castable, reactive liquids, which react to form a urethane elastomer material, provide desirable very thin outer cover layers.

The castable, reactive liquid employed to form the urethane elastomer material can be applied over the core using a variety of application techniques such as spraying, dipping, spin coating, or flow coating methods which are well known in the art. An example of a suitable coating technique is that which is disclosed in U.S. Pat. No. 5,733,428, the disclosure of which is hereby incorporated by reference in its entirety in the present application.

The outer cover is preferably formed around the inner cover by mixing and introducing the material in the mold halves. It is important that the viscosity be measured over time, so that the subsequent steps of filling each mold half, introducing the core into one half and closing the mold can be properly timed for accomplishing centering of the core cover halves fusion and achieving overall uniformity. Suitable viscosity range of the curing urethane mix for introducing cores into the mold halves is determined to be approximately between about 2,000 cP and about 30,000 cP, with the preferred range of about 8,000 cP to about 15,000 cP.

To start the cover formation, mixing of the prepolymer and curative is accomplished in motorized mixer including mixing head by feeding through lines metered amounts of curative and prepolymer. Top preheated mold halves are filled and placed in fixture units using centering pins moving into holes in each mold. At a later time, a bottom mold half or a series of bottom mold halves have similar mixture amounts introduced into the cavity. After the reacting materials have resided in top mold halves for about 40 to about 80 seconds, a core is lowered at a controlled speed into the gelling reacting mixture.

A ball cup holds the ball core through reduced pressure (or partial vacuum). Upon location of the coated core in the halves of the mold after gelling for about 40 to about 80 seconds, the vacuum is released allowing core to be released. The mold halves, with core and solidified cover half thereon, are removed from the centering fixture unit, inverted and mated with other mold halves which, at an appropriate time earlier, have had a selected quantity of reacting polyurethane prepolymer and curing agent introduced therein to commence gelling.

Similarly, U.S. Pat. No. 5,006,297 and U.S. Pat. No. 5,334,673 both also disclose suitable molding techniques which may be utilized to apply the castable reactive liquids employed in the present invention. Further, U.S. Pat. Nos. 6,180,040 and 6,180,722 disclose methods of preparing dual core golf balls. The disclosures of these patents are hereby incorporated by reference in their entirety. However, the method of the invention is not limited to the use of these techniques.

The molding process and composition of golf ball portions typically results in a gradient of material properties. Methods employed in the prior art generally exploit hardness to quantify these gradients. Hardness is a qualitative measure of static modulus and does not represent the modulus of the material at the deformation rates associated with golf ball use, i.e., impact by a club. As is well known to one skilled in the art of polymer science, the time-temperature superposition principle may be used to emulate alternative

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deformation rates. For golf ball portions including polybutadiene, a 1-Hz oscillation at temperatures between 0° C. and -50° C. are believed to be qualitatively equivalent to golf ball impact rates. Therefore, measurement of loss tangent and dynamic stiffness at 0° C. to -50° C. may be used to accurately anticipate golf ball performance, preferably at temperatures between about -20° C. and -50° C.

The resultant golf balls typically have a coefficient of restitution of greater than about 0.7, preferably greater than about 0.75, and more preferably greater than about 0.78. The golf balls also typically have an Atti compression of at least about 40, preferably from about 50 to 120, and more preferably from about 60 to 100. The golf ball cured polybutadiene material typically has a hardness of at least about 15 Shore A, preferably between about 30 Shore A and 80 Shore D, more preferably between about 50 Shore A and 60 Shore D.

When golf balls are prepared according to the invention, they typically will have dimple coverage greater than about 60 percent, preferably greater than about 65 percent, and more preferably greater than about 75 percent. The flexural modulus of the cover on the golf balls, as measured by ASTM method D6272-98, Procedure B, is typically greater than about 500 psi, and is preferably from about 500 psi to 150,000 psi. As discussed herein, the outer cover layer is preferably formed from a relatively soft polyurethane material. In particular, the material of the outer cover layer should have a material hardness, as measured by ASTM-D2240, less than about 45 Shore D, preferably less than about 40 Shore D, more preferably between about 25 and about 40 Shore D, and most preferably between about 30 and about 40 Shore D. The casing preferably has a material hardness of less than about 70 Shore D, more preferably between about 30 and about 70 Shore D, and most preferably, between about 50 and about 65 Shore D.

It should be understood, especially to one of ordinary skill in the art, that there is a fundamental difference between "material hardness" and "hardness, as measured directly on a golf ball." Material hardness is defined by the procedure set forth in ASTM-D2240 and generally involves measuring the hardness of a flat "slab" or "button" formed of the material of which the hardness is to be measured. Hardness, when measured directly on a golf ball (or other spherical surface) is a completely different measurement and,

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and/or cover layers, etc.), ball (or sphere) diameter, and the material composition of adjacent layers. It should also be understood that the two measurement techniques are not linearly related and, therefore, one hardness value cannot easily be correlated to the other.

The core of the present invention has an Atti compression of less than about 80, more preferably, between about 40 and about 80, and most preferably, between about 50 and about 70. In an alternative, low compression embodiment, the core has a compression less than about 20, more preferably less than about 10, and most preferably, 0. The overall outer diameter ("OD") of the core is less than about 1.610 inches, preferably, no greater than 1.590 inches, more preferably between about 1.540 inches and about 1.580 inches, and most preferably between about 1.50 inches to about 1.570 inches. The OD of the casing of the golf balls of the present invention is preferably between 1.580 inches and about 1.640 inches, more preferably between about 1.590 inches to about 1.630 inches, and most preferably between about 1.600 inches to about 1.630 inches.

The present multilayer golf ball can have an overall diameter of any size. Although the United States Golf Association ("USGA") specifications limit the minimum size of a competition golf ball to 1.680 inches. There is no specification as to the maximum diameter. Golf balls of any size, however, can be used for recreational play. The preferred diameter of the present golf balls is from about 1.680 inches to about 1.800 inches. The more preferred diameter is from about 1.680 inches to about 1.760 inches. The most preferred diameter is about 1.680 inches to about 1.740 inches.

EXAMPLE

35 Three solid cores, each having an outer diameter of 1.58 inches, were formed of a composition comprising polybutadiene rubber, zinc diacrylate, zinc oxide, dicumyl peroxide, barium sulfate, and color dispersion. One core, representative of conventional technology, was used as a control. The 40 two remaining cores were each additionally blended with 5.3 parts Struktol® (Example 1) and the zinc salt of pentachlorothiophenol at 2.4 parts (Example 2). Struktol® at 5.3 parts contains 2.4 parts PCTP. The specific compositions for each of the solid cores are presented below in Table I.

TABLE I

INGREDIENT	CONTROL				EXAMPLE 1				EXAMPLE 2			
	100	100	100	100	100	100	100	100	100	100	100	100
polybutadiene rubber	100	100	100	100	100	100	100	100	100	100	100	100
zinc diacrylate	18	25	30	27	34	41	20	25	30	35		
dicumyl peroxide	0.5	0.5	0.5	1.8	1.8	1.8	0.8	0.8	0.8	0.8	0.8	0.8
Struktol® A95	—	—	—	5.3	5.3	5.3	—	—	—	—	—	—
zinc salt of PCTP	—	—	—	—	—	—	2.4	2.4	2.4	2.4	2.4	2.4
zinc oxide	26.5	24.1	22.2	5	5	5	5	5	5	5	5	5
barium sulfate	—	—	—	16.2	13.4	10.6	21.7	19.7	17.7	15.7		
color dispersion	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14
PROPERTY												
Effective Modulus (psi)	3800	6200	8700	4100	6200	7700	3600	5100	7400	9700		
Atti Compression COR @ 125 ft/s	17 0.764	52 0.789	76 0.802	22 0.773	52 0.794	67 0.802	13 0.782	38 0.801	65 0.813	84 0.823		

therefore, results in a different hardness value. This difference results from a number of factors including, but not limited to, ball construction (i.e., core type, number of core

65 It is very apparent that the addition of PCTP, in either form, increases COR, decreases compression, or both. In particular, the PCTP zinc salt (Example 2) provides com-

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parable COR's with lower compression and/or increased COR's with comparable (or lower) compression, both of which are desirable golf ball properties.

The halogenated organosulfur polymers of the present invention may also be used in golf equipment, in particular, inserts for golf clubs, such as putters, irons, and woods, and in golf shoes and components thereof.

As used herein, the term "about," used in connection with one or more numbers or numerical ranges, should be understood to refer to all such numbers, including all numbers in a range.

The invention described and claimed herein is not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Any equivalent embodiments are intended to be within the scope of this invention. Indeed, various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

What is claimed is:

1. A golf ball having a core and a cover, wherein the core has a compression of less than about 75 and a diameter of at least about 1.50 inches and comprises a polybutadiene rubber composition comprising at least about 2.2 parts per hundred of a halogenated organosulfur compound, and wherein the golf ball has a coefficient of restitution of greater than about 0.800 and the cover has a thickness of less than about 0.1 inches and comprises a polyurethane composition.

2. The golf ball of claim 1, wherein the core comprises a center and an outer core layer.

3. The golf ball of claim 1, wherein the core has a diameter of at least about 1.55 inches.

4. The golf ball of claim 1, wherein the cover comprises an inner cover layer and an outer cover layer.

5. The golf ball of claim 4, wherein at least one of the inner and outer cover layers have a thickness of less than about 0.05 inches.

6. The golf ball of claim 5, wherein the inner cover layer comprises an ionomeric material, vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, polycarbonates, polybutylene terephthalates, acrylonitriles, butadienes, or partially-neutralized polymers.

7. The golf ball of claim 1, wherein the polybutadiene rubber composition comprises between about 2.2 parts and about 5 parts of a halogenated organosulfur compound.

8. The golf ball of claim 1, wherein the halogenated organosulfur compound is selected from the group consisting of pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol; 2,3,4-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol; 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-

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bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2,3-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof and mixtures thereof.

9. The golf ball of claim 8, wherein the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof.

10. The golf ball of claim 9, wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium.

11. The golf ball of claim 10, wherein the metal salt is zinc.

12. The golf ball of claim 1, wherein the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

13. The golf ball of claim 1, wherein the golf ball has a coefficient of restitution of greater than about 0.815.

14. The golf ball of claim 1, wherein the core has a compression of less than about 55 and the golf ball has a coefficient of restitution of greater than about 0.815.

15. The golf ball of claim 1, wherein the polybutadiene composition further comprises an α,β -unsaturated carboxylic acid or a metal salt thereof, an organic peroxide, and a filler.

16. The golf ball of claim 1, wherein the polyurethane composition comprises a prepolymer formed of a polyisocyanate and a polyol, and a curing agent.

17. The golf ball of claim 16, wherein at least one of the prepolymer and curing agent is saturated.

18. A golf ball formed of a single core and a cover, wherein the core has a diameter of at least about 1.55 inches and comprises a polybutadiene rubber composition comprising greater than about 2.3 parts per hundred of pentachlorothiophenol or a metal salt thereof, and wherein the cover comprises:

an inner cover layer comprising an ionomeric material and having a thickness of less than about 0.04 inches; and
an outer cover layer having a thickness of no greater than about 0.03 inches and comprising a polyurethane composition.

19. A golf ball formed of a core and a cover, wherein the core has a compression of less than about 75 and a diameter of at least about 1.50 incline and comprises a polybutadiene rubber composition comprising at least about 2.2 parts per hundred of a halogenated organosulfur compound, and wherein the golf ball has a coefficient of restitution of greater than about 0.800 and the cover has a thickness of less than about 0.1 inches and is formed of an inner cover layer and an outer cover layer.

20. The golf ball of claim 19, wherein the core comprises a center having an outer diameter of at least about 1.55 inches and an outer core layer.

21. The golf ball of claim 19, wherein at least one of the inner and outer cover layers has a thickness of less than about 0.05 inches.

22. The golf ball of claim 19, wherein at least one of the cover layers comprises vinyl resins, polyolefins, polyurethanes, polyureas, polyamides, acrylic resins, thermoplastics, polyphenylene oxide resins, thermoplastic polyesters, thermoplastic rubbers, fully-neutralized polymers, polycarbonates, polybutylene terephthalates, acrylonitriles, butadienes, or partially-neutralized polymers.

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23. The golf ball of claim 19, wherein the polybutadiene rubber composition comprises between about 2.2 parts and about 5 parts of a halogenated organosulfur compound.

24. The golf ball of claim 23, wherein the halogenated organosulfur compound is selected from the group consisting of pentafluorothiophenol; 2-fluorothiophenol; 3-fluorothiophenol; 4-fluorothiophenol; 2,3-fluorothiophenol; 2,4-fluorothiophenol; 3,4-fluorothiophenol; 3,5-fluorothiophenol 2,3,4-fluorothiophenol; 3,4,5-fluorothiophenol; 2,3,4,5-tetrafluorothiophenol; 2,3,5,6-tetrafluorothiophenol; 4-chlorotetrafluorothiophenol; pentachlorothiophenol; 2-chlorothiophenol; 3-chlorothiophenol; 4-chlorothiophenol; 2,3-chlorothiophenol; 2,4-chlorothiophenol; 3,4-chlorothiophenol; 3,5-chlorothiophenol; 2,3,4-chlorothiophenol; 3,4,5-chlorothiophenol; 2,3,4,5-tetrachlorothiophenol; 2,3,5,6-tetrachlorothiophenol; pentabromothiophenol; 2-bromothiophenol; 3-bromothiophenol 4-bromothiophenol; 2,3-bromothiophenol; 2,4-bromothiophenol; 3,4-bromothiophenol; 3,5-bromothiophenol; 2,3,4-bromothiophenol; 3,4,5-bromothiophenol; 2,3,4,5-tetrabromothiophenol; 2,3,5,6-tetrabromothiophenol; pentaiodothiophenol; 2-iodothiophenol; 3-iodothiophenol; 4-iodothiophenol; 2,3-iodothiophenol; 2,4-iodothiophenol; 3,4-iodothiophenol; 3,5-iodothiophenol; 2,3,4-iodothiophenol; 3,4,5-iodothiophenol; 2,3,4,5-tetraiodothiophenol; 2,3,5,6-tetraiodothiophenol; and their zinc salts, the metal salts thereof and mixtures thereof.

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25. The golf ball of claim 24, wherein the halogenated organosulfur compound is pentachlorothiophenol or the metal salt thereof.

26. The golf ball of claim 25, wherein the metal salt is selected from the group consisting of zinc, calcium, magnesium, sodium, and lithium.

27. The golf ball of claim 26, wherein the metal salt is zinc.

28. The golf ball of claim 19, wherein the golf ball has a coefficient of restitution of greater than about 0.815.

29. The golf ball of claim 19, wherein the core has a compression less than about 55 and the golf ball has a coefficient of restitution of greater than about 0.815.

30. The golf ball of claim 19, wherein the polybutadiene composition further comprises an α,β -unsaturated carboxylic acid or a metal salt thereof an organic peroxide, and a filler.

31. The golf ball of claim 19, wherein the outer cover layer is formed of a polyurethane composition comprising a prepolymer formed of a polyisocyanate and a polyol, and a curing agent.

32. The golf ball of claim 31, wherein at least one of the prepolymer and curing agent are saturated.

33. The golf ball of claim 31, wherein the polyurethane composition comprises at least one of a UV absorber, a hindered amine light stabilizer, or an optical brightener.

* * * * *

EXHIBIT 10



US005605968A

United States Patent [19]
Egashira et al.

[11] Patent Number: **5,605,968**
[45] Date of Patent: **Feb. 25, 1997**

[54] GOLF BALL

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[21] Appl. No.: **447,044**[22] Filed: **May 22, 1995****Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 213,587, Mar. 16, 1994, abandoned.

[30] Foreign Application Priority Data

Mar. 17, 1993 [JP] Japan 5-082714

[51] Int. Cl.⁶ A63B 37/12; A63B 37/06;

C08L 23/08; C08L 33/02

[52] U.S. Cl. 525/221; 525/196; 525/195;

524/908; 473/385; 473/367; 473/372

[58] Field of Search 525/195, 196, 525/221; 524/908; 273/235 R, 230; 473/385, 367, 372

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[57] ABSTRACT

A solid golf ball includes a solid core enclosed in a cover. The resin component of the cover consists of 30 to 100% by weight of an ethylene-methacrylic acid-acrylate terpolymer ionomer resin having a flexural modulus of 2,500–14,000 psi and a Shore D hardness of 20–59 and 70 to 0% by weight of an ethylene-(meth)acrylic acid copolymer ionomer resin having a flexural modulus of 20,000–29,000 psi and a Shore D hardness of 56–62. The ball is excellent in spin receptivity, buring resistance, and feel on hitting.

3 Claims, No Drawings

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GOLF BALL**CROSS REFERENCE TO RELATED APPLICATION**

This application is a continuation-in-part of application Ser. No. 08/213,587 filed on Mar. 16, 1994, now abandoned the entire contents of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTION**1. Field of the Invention**

This invention relates to a solid golf ball which is improved in ball control, feel on hitting, spin receptivity, durability, and flying performance.

2. Prior Art

Because of their impact durability and cut resistance, ionomer resins in the form of ethylene-(meth)acrylic acid copolymers have been widely used and accepted as the cover material for most two-piece golf balls and some wound golf balls. It is, however, said that golf balls with ionomer resin covers are difficult to give a spin as intended when hit by an iron and thus relatively poor in ball control probably because the ionomer resins offer a harder feel on hitting and have higher hardness than balata rubber which is a conventional cover material.

It was thus proposed to use a blend of soft and hard ionomer resins as the golf ball cover as disclosed in U.S. Pat. No. 4,884,814 and JP-A 308577/1989. More particularly, an ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer having a certain spectrum of physical properties is blended with a relatively soft ionomer resin in the form of an ethylene-(meth)acrylic acid-(meth)acrylate terpolymer. While the golf balls using an ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer as the cover suffered from hard hitting feel and difficult ball control, the use of such a blend was effective for achieving significant improvements in these properties.

The golf ball cover of a soft and hard ionomer blend by this proposal, however, has the following problems. The fact that the cover is softer and more receptive to spin on an iron shot indicates an increased frictional force between the club face and the cover. Then balls using a hard core like two-piece golf balls tend to be burred or finely split on the surface since the cover surface can be ablated or scraped by the iron club grooves on an iron shot.

In addition, the ionomer cover itself is low in repulsion due to low hardness, resulting in a substantial loss of ball repulsion.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a solid golf ball which is satisfactory in feel on hitting, spin receptivity, ball control, and burring resistance, while maintaining the flying distance inherent to solid golf balls such as two-piece golf balls.

Attempting to produce a solid golf ball which has a soft feel, good spin receptivity, and acceptable repulsion, and is improved in resistance against burring or fine splitting on an iron shot, the inventors have found that as compared with the

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conventional blend of hard and soft ionomer resins, a blend of a mid-hardness ionomer resin having an intermediate hardness between hard and soft ionomer resins and a soft ionomer resin or a soft ionomer resin alone experiences significantly less surface damage on an iron shot. Balls with a cover which is more resistant against burring on the surface are also satisfactory in feel and spin properties. However, the cover as such is soft and thus low repulsive. It is then difficult to utilize this cover in golf balls. Quite unexpectedly, the above-mentioned requirements can be effectively met by combining the cover with a special core. By blending pentachlorothiophenol or a metal salt thereof in base rubber, a more repulsive core is obtained so that the resulting ball provides a satisfactory level of repulsion.

The present invention provides a golf ball comprising a solid core and a cover enclosing the core. The cover is based on a resin component consisting of (1) 30 to 100% by weight of a first ionomer resin in the form of an ethylene-methacrylic acid-acrylate terpolymer having a flexural modulus of 2,500 to 14,000 psi and a Shore D hardness of 20 to 59 and (2) 70 to 0% by weight of a second ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer having a flexural modulus of 20,000 to 29,000 psi and a Shore D hardness of 56 to 62. The core is preferably made of a rubber composition comprising 100 parts by weight of a base rubber and 0.2 to 1.5 parts by weight of pentachlorothiophenol or a metal salt thereof and has a distortion of 2.3 to 3.3 mm under a load of 100 kg.

DETAILED DESCRIPTION OF THE INVENTION

The golf ball of the present invention has a generally spherical solid core enclosed in a cover. The cover is essentially made of a blend of (1) 30 to 100% by weight, preferably 50 to 90% by weight of a first ionomer resin in the form of an ethylene-methacrylic acid-acrylate terpolymer and (2) 70 to 0% by weight, preferably 50 to 10% by weight of a second ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer.

In the first ionomer resin in the form of an ethylene-methacrylic acid-acrylate terpolymer, the acrylate should preferably have 4 to 12 carbon atoms. Examples of acrylate include methyl acrylate, ethyl acrylate, isobutyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate. Among them, isobutyl acrylate is preferred. The terpolymer should preferably contain 5 to 15% by weight, preferably 7 to 12% by weight of methacrylic acid, 5 to 45% by weight, preferably 8 to 30% by weight of the acrylate, and the balance of ethylene. With more than 15% by weight of methacrylic acid, a soft cover would not be obtained. With less than 5% by weight of methacrylic acid, repulsion of a golf ball would be lowered. With more than 45% by weight of the acrylate, burring resistance would become inferior because of a too soft cover. With less than 5% by weight of the acrylate, a soft cover would not be obtained. The (meth)acrylic acid in the terpolymer is neutralized with metal ion, preferably zinc ion or sodium ion in an amount of 10 to 90 mol %, preferably 30 to 80 mol % of the (meth)acrylic acid to form an ionomer resin. If the neutralization degree is less than 10 mol %, repulsion of a golf ball would be lowered. If the neutraliza-

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tion degree is more than 90 mol %, the fluidity of a resin composition upon molding would be worsened.

In the second ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer, the content of (meth)acrylic acid should preferably be in the range of 5 to 12% by weight, more preferably 8 to 11% by weight. With more than 12% by weight of (meth)acrylic acid, a soft ionomer resin would not be obtained and thus a soft cover could not be formed. With less than 8% by weight of (meth)acrylic acid, repulsion would be insufficient. The (meth)acrylic acid in the copolymer is neutralized with a metal ion, preferably zinc ion or sodium ion in an amount of 10 to 90 mol %, preferably 30 to 80 mol % of the (meth)acrylic acid. If the neutralization degree is less than 10 mol %, repulsion would be insufficient. If the neutralization degree is more than 90 mol %, the fluidity of a resin composition upon molding would be worsened.

The first ionomer resin in the form of an ethylene-methacrylic acid-acrylate terpolymer has a flexural modulus of 2,500 to 14,000 psi and a Shore D hardness of 20 to 59 and is commercially available in the trade names of Himilan from Du Pont-Mitsui Polymers Co., Ltd. and Surlyn from E. I. duPont as shown in Table 1. The second ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer has a flexural modulus of 20,000 to 29,000 psi, preferably 20,000 to 28,500 psi, more preferably 20,000 to 28,000 psi and a Shore D hardness of 52 to 62 and is commercially available in the trade name of Himilan from DUPONT-MITSUI POLYCHEMICALS CO. LTD. as shown in Table 2.

TABLE 1

		Flexural modulus (psi)	Shore D hardness
	Ion		
Himilan 1855	Zn	13,000	56
Himilan 1856	Na	10,100	58
Surlyn 8120	Na	7,100	39
Surlyn 8320	Na	2,800	25

TABLE 2

		Flexural modulus (psi)	Shore D hardness
	Ion		
Himilan 1650	Zn	24,700	60
Himilan 1652	Zn	23,000	57
Himilan 1702	Zn	21,700	62

In addition to the resin component, the resin composition for the cover may contain optional additives, for example, dyestuffs, pigments such as titanium dioxide, zinc oxide, and barium sulfate, UV absorbers, anti-oxidants, and dispersing aids such as metal soaps. The ionomer resins and optional additives are mixed in a conventional mixer such as a closed kneader (e.g., Bunnay mixer and kneader) and an extruder and then molded in a conventional manner.

The core is made of a rubber composition comprising a base rubber, a metal salt of an unsaturated carboxylic acid, and a peroxide. Preferably, pentachlorothiophenol or a metal salt thereof is added to the above rubber composition.

The base rubber is preferably cis-1,4-polybutadiene rubber containing at least 90% of cis-configuration because of

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its high repulsion. Although another rubber component such as natural rubber and polyisoprene rubber may be blended in the cis-1,4-polybutadiene rubber, it is preferred that the base rubber contains at least 80% by weight of the high cis-1,4-polybutadiene rubber. With less than 80% by weight of high cis-1,4-polybutadiene rubber, the base rubber would not take full advantage of the repulsion thereof. The metal salt of an unsaturated carboxylic acid such as acrylic acid and methacrylic acid is blended as a co-crosslinking agent, preferably in an amount of about 25 to 40 parts by weight per 100 parts by weight of the base rubber. Examples of the metal salt of an unsaturated carboxylic acid include zinc salts, magnesium salts and calcium salts of acrylic acid or methacrylic acid. Among them, zinc acrylate is most preferred. The peroxide includes dicumyl peroxide, t-butylperoxybenzoate, di-t-butylperoxide, and 1,1-bis(t-butylperoxy)-3,3,5-trimethyl-cyclohexane. Preferably the peroxide is blended in an amount of about 0.5 to 3 parts, more preferably 0.8 to 2 parts by weight per 100 parts by weight of the base rubber. It is preferable to add pentachlorothiophenol or its salt to the composition for improving repulsion of a golf ball. Pentachlorothiophenol or its salt is blended in an amount of about 0.2 to 1.5 parts by weight per 100 parts by weight of the base rubber in order that this blend system be enhanced in repulsion. Beyond this range, the rubber composition for the core can be retarded in crosslinking reaction. Examples of the salt include zinc salt of pentachlorothiophenol.

If desired, the rubber composition for the core may contain any additive commonly used in the core of two-piece solid golf balls, for example, zinc oxide, anti-oxidant, and barium sulfate. The core rubber composition is mixed in a conventional mixer such as a Bunnay mixer and kneader and then molded and cured into a spherical core by hot pressure vulcanization in a conventional manner. The vulcanized composition or core should have a hardness in a specific range. That is, the distortion of the core under a load of 100 kg should be 2.3 to 3.3 mm. With a distortion of less than 2.3 mm, a ball after enclosure in a cover as defined above is hard and gives an unpleasant hitting feel. With a distortion of more than 3.3 mm, the resulting ball is less repulsive.

The golf ball of the invention is prepared by conventional processes, for example, by molding a solid core from a core material, forming leaf cups from a cover material by a conventional molding technique, and enclosing the core with the leaf cups followed by heat compression molding. Alternatively the solid core is directly covered with a cover material by injection molding.

The thickness of the cover is in the range of 1.4 to 2.5 mm. The diameter of the golf ball is 42.67 mm or more and the weight of the golf ball is 45.93 g or less.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

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A solid core was formed from a rubber composition of the following components.

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TABLE 3-continued

Component	Parts by weight
cis-1,4-polybutadiene rubber (BR01)	100
zinc acrylate	33.5
zinc oxide	10
barium sulfate	9.6
anti-oxidant	0.2
dicumyl peroxide	0.9

The solid core was directly covered by injection molding with a cover material consisting of ionomer resin, titanium dioxide for coloring, and dispersing aids, and having a specific gravity of 0.99. The ionomer resins used were Himilan and Surlyn resins having physical properties as shown in Table 3. They were mixed as shown in Table 4. The cover was surface treated and coated with clear lacquer. The resulting two-piece golf balls were measured for weight (g), surface hardness (Shore C and D scales), distortion (mm under a load of 100 kg) and initial speed (m/sec.).

Designation	Ion type	MER	Elongation (%)	Flexural modulus (psi)	Shore D hardness
Himilan 1650	Zn	1.5	460	24,700	60
Himilan 1652	Zn	5.0	500	23,000	57
Himilan 1855	Zn	1.0	510	13,000	56
Himilan 1856	Na	1.0	530	10,100	58
Surlyn 8120	Na	0.9	660	7,100	39
Surlyn 8320	Na	0.9	770	2,800	25
Surlyn 9970	Zn	14.0	460	28,000	62

A burring test was carried out on the balls using a robot machine equipped with three pitching wedges, Eagle PW, Rextar HT305 PW and MSX PW commercially available from Bridgestone Sports Co., Ltd. A ball was hit at three different points, once at each point, by each pitching wedge at a head speed of 37 m/s. The three hit points on the ball were visually observed and evaluated in accordance with the following criteria.

- : slight, substantially unnoticeable club face mark
 - Δ: distinct club face mark, but not feathered on cover surface
 - ×: surface burred and noticeably feathered
- The results are also shown in Table 4.

TABLE 4

Cover resin mix	Inventive Cover									Comparative Cover				
	1	2	3	4	5	6	7	8	9	1	2	3	4	5
Himilan 1706 (Zn)										50	50	25		
Himilan 1557 (Zn)										50	50			
Surlyn 9970 (Zn)													75	75
Himilan 1650 (Zn)	50	50	50	25		30								
Himilan 1652 (Zn)				25	50									
Himilan 1702 (Zn)														
Himilan 1855 (Zn)							50							
Himilan 1856 (Zn)	50					50	50							
Surlyn 8120 (Na)		50		50	50	70				50	50	50		25
Surlyn 8320 (Na)			50								50			
<u>Ball properties</u>														
Weight (g)	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2	45.2
Surface Shore C		82		79	76									
hardness Shore D	60	57	49	55	53	51	58	60	58	59	58	53	61	59
Distortion (mm)	2.39	2.43	2.57	2.47	2.44	2.52	2.40	2.38	2.43	2.37	2.38	2.40	2.30	2.36
Initial speed (m/sec.)	77.09	76.83	76.57	76.81	76.59	76.62	76.80	77.02	76.83	77.22	77.26	76.10	77.15	77.01
<u>Burring test</u>														
Eagle PW	○ or Δ	○	○	○ or Δ	○ or Δ	○	○ or Δ	○ or X	Δ	X	X	Δ		
Rextar HT305 PW	○ or Δ	○	○	○ or Δ	○	○	○ or Δ	○ or X	Δ	X	X	Δ		
MSX PW	○	○	○	○	○	○	○	○ or Δ	Δ	Δ or X	X	Δ or X	Δ	

The thickness of the cover was 2.0 mm. The diameter of the golf ball was 42.7 mm and the weight of the golf ball was 45.2 g.

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It is evident from Table 4 that the covers of the present invention are fully resistant against burring by the iron club face.

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Next, cores (the diameter 38.7 mm) were molded from the compositions shown in Table 5 and measured for a distortion (mm) under a load of 100 kg and initial speed (m/sec.). The core initial speed was measured using an initial speed meter of the same type as prescribed by golf ball authorized organization R&A (USGA). The results are also shown in Table 5.

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TABLE 3

Designation	Ion type	MER	Elongation (%)	Flexural modulus (psi)	Shore D hardness
Himilan 1706	Zn	0.7	290	47,900	66
Himilan 1577	Zn	5.0	410	36,300	63

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TABLE 5

Control Core	Inventive Core					
	1	1	2	3	4	5
<u>Composition</u>						
BRO1	100	100	100	100	100	100
Zinc acrylate	33.5	33.5	33.5	33.5	33.5	33.5
Barium sulfate	9.6	9.6	9.6	9.6	9.6	9.6
Zinc oxide	10	10	10	10	10	10
Anti-oxidant	0.2	0.2	0.2	0.2	0.2	0.2
Lenacit IV*	—	0.2	0.4	0.6	1.0	1.5
Dicumyl peroxide	0.9	0.9	0.9	0.9	0.9	0.9
<u>Vulcanized core properties</u>						
Distortion (mm)	2.61	2.51	2.62	2.64	2.67	2.71
Initial speed	77.75	78.14	78.29	78.35	78.64	78.54

*zinc salt of pentachlorothiophenol commercially available from Bayer Japan Ltd.

It is evident from Table 5 that the cores of the present invention offer an increased initial speed which indicates improved repulsion.

Next, two-piece golf balls were prepared by combining the cover and the core as shown in Table 6. The balls were measured for initial speed by the same procedure as above. The balls were also determined for back spin, stop on the green, and driver flying distance by the following tests. The thickness of the cover was 2.0 mm.

Back Spin

Using a swing robot manufactured by True Temper Co., the ball was hit by an iron (pitching wedge) at a head speed of 37 m/s. The spin quantity was measured by taking a photograph of the ball immediately after impact followed by image analysis.

Stop on the Green

Using the swing robot, the ball was hit by a pitching wedge so as to fly directly on the green. The distance between the landing and stop positions, which was the distance the ball covered due to back spin, was measured.

Flying Distance

Using the swing robot, the ball was hit by a driver W#1 at a head speed of 45 m/s to measure the flying distance.

The results are shown in Table 6.

TABLE 6

	Inventive core				Comparative	Commercial 2-piece
	No. 1 Himilan 1650/ Surlyn 8120 50/50	No. 4 Himilan 1650/ Surlyn 8120 50/50	No. 4 Himilan 1855/ Surlyn 1856 50/50	No. 1 Himilan 1650/ Surlyn 8120 50/50		
Initial speed (m/s)	77.08	77.30	77.27	76.85	77.10	
Back	9350	9280	9310	9290	8750	

TABLE 6-continued

25	Inventive core				Comparative	Commercial 2-piece
	No. 1 Himilan 1650/ Surlyn 8120 50/50	No. 4 Himilan 1650/ Surlyn 8120 50/50	No. 4 Himilan 1855/ Surlyn 1856 50/50	No. 1 Himilan 1650/ Surlyn 8120 50/50		
spin (rpm)						
Stop on the green (m)	0.0	0.5	0.5	0.5	3.5	
Driver flying distance	225.0	224.5	225.5	220.5	225.0	

As is evident from Table 6, the golf balls of the invention are excellent in ball control and flying performance.

The golf balls of the invention are excellent in spin characteristics, burning resistance, and repulsion.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

We claim:

- A golf ball comprising a solid core and a cover enclosing the core, wherein said cover is based on a resin component consisting of 30 to 90% by weight of a first ionomer resin in the form of an ethylene-methacrylic acid-acrylate terpolymer having a flexural modulus of 10,000 to 14,000 psi and a Shore D hardness of 56 to 59 and 70 to 10% by weight of a second ionomer resin in the form of an ethylene-(meth)acrylic acid copolymer having a flexural modulus of 20,000 to 29,000 psi and a Shore D hardness of 56 to 62.
- The golf ball of claim 1 wherein said core is made of a rubber composition comprising 100 parts by weight of a base rubber and 0.2 to 1.5 parts by weight of penta-

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chlorothiophenol or a metal salt thereof and has a distortion of 2.3 to 3.3 mm under a load of 100 kg.

3. The golf ball of claim 1 wherein the first ionomer resin is blended in an amount of 50 to 90% by weight and the

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second ionomer resin is blended in an amount of 50 to 10% by weight.

* * * * *

EXHIBIT 11



US006679791B2

(12) **United States Patent**
Watanabe

(10) Patent No.: **US 6,679,791 B2**
(45) Date of Patent: **Jan. 20, 2004**

(54) **GOLF BALL**

(75) Inventor: Hideo Watanabe, Chichibu (JP)

(73) Assignee: Bridgestone Sports Co., Ltd., Tokyo (JP)

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(74) Attorney, Agent, or Firm—Sughrue Mion, PLLC

(57) ABSTRACT

A multi-piece golf ball includes a rubbery elastic core, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof. The center and surface of the elastic core have a hardness difference of at least 18 JIS-C hardness units. This construction and combination of features improve the distance of the ball when struck with a driver, provide the ball with excellent spin characteristics and thus good controllability on approach shots, and gives the ball a good feel on impact, enabling the ball to meet the high expectations of skilled golfers.

27 Claims, 1 Drawing Sheet

(21) Appl. No.: **09/880,844**(22) Filed: **Jun. 15, 2001**

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(51) Int. Cl.⁷ A63B 37/04; A63B 37/06; A63B 37/00

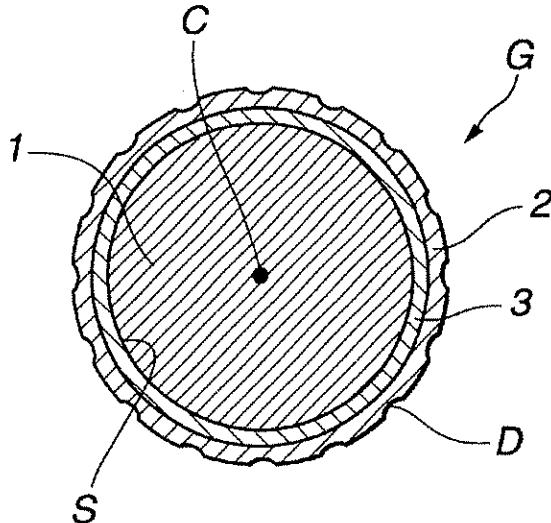
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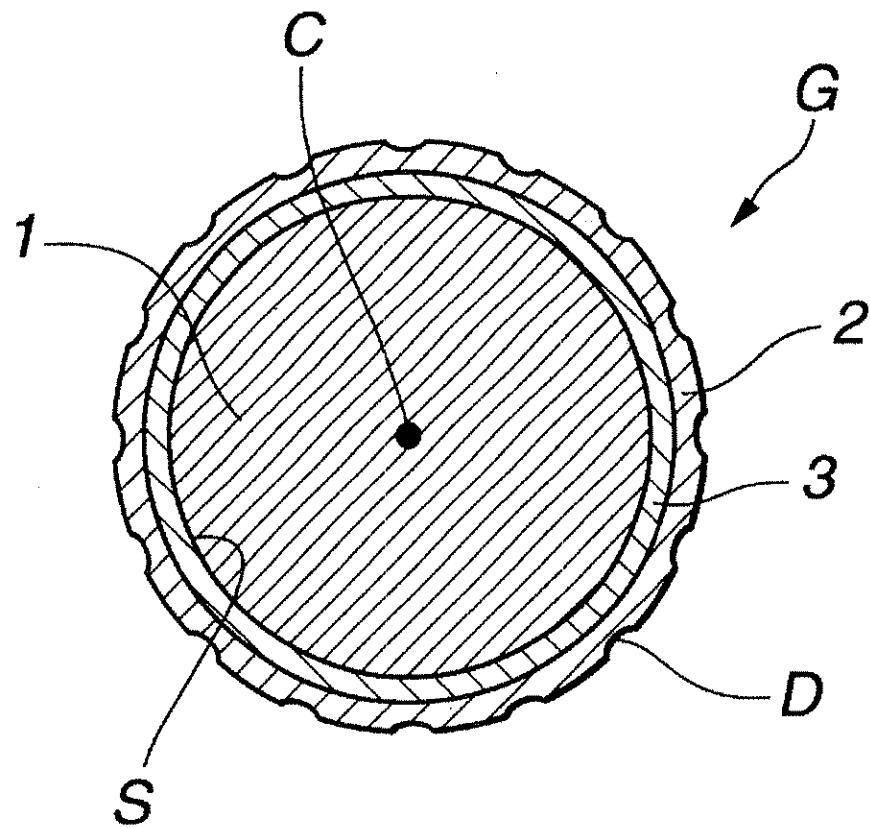


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FIG. 1



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GOLF BALL**BACKGROUND OF THE INVENTION****1. Field of the Invention**

The present invention relates to a golf ball having a multilayer construction of at least three layers which includes a core, an intermediate layer and a cover. More particularly, the invention relates to a golf ball which has good rebound characteristics and provides an excellent travel distance, controllability and "feel" upon impact with a golf club.

2. Prior Art

In recent years, solid golf balls, with their good flight performance, have consistently won greater general approval than conventional thread-wound golf balls.

Solid golf ball constructions include two-piece balls made of a solid, high-resilience, rubber core enclosed within a relatively thin resin cover, and multi-piece balls having a core, a cover, and also an intermediate layer therebetween whose properties differ somewhat from those of the cover.

As already noted, because of their good flight performance (i.e., long travel distance), solid golf balls of these types are widely favored by both amateur and professional golfers. Yet, there remains a desire among golfers for even better flight performance.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a golf ball having a multilayer construction of three or more layers that is endowed with improved distance without diminishing the controllability and feel that are so important to skilled golfers.

Accordingly, the invention provides a golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover. The intermediate layer is composed of a resin material which is harder than the cover. The elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 18 between the center and the surface.

Preferably, the JIS-C hardness at the center of the core is 50 to 65, and the JIS-C hardness at the surface of the core is 70 to 90. The core typically undergoes a deformation of 3.0 to 5.0 mm when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

BRIEF DESCRIPTION OF THE DRAWING

The objects, features and advantages of the invention will become more apparent from the following detailed description, taken in conjunction with the accompanying diagram.

The only FIGURE, FIG. 1 is a sectional view showing a golf ball according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, the golf ball G of the present invention has a construction composed of at least three layers, commonly known as a "multi-piece construction," which include a rubbery elastic core 1, a cover 2 that is

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generally made of a resin material and has a plurality of dimples D on the surface thereof, and one or more intermediate layer 3 between the core 1 and the cover 2, all situated in a concentric fashion. The illustrated embodiment has a single intermediate layer. The intermediate layer 3 is made of a resin material which is harder than the cover 2. The core 1 having a center C and a surface S at its radially outer extremity has a JIS-C hardness which gradually increases radially outward from the center C to the surface S. The core 1 is formed so as to have a specific hardness difference between the surface S and the center C.

The inventive golf ball includes a hard intermediate layer disposed between the core, which has an optimized hardness profile, and the cover which is softer than the intermediate layer. This construction provides the ball with an excellent "feel," holds down spin when the ball is struck with a driver, and increases the distance traveled, in part by creating a trajectory which does not describe a high arc when traveling into a headwind. At the same time, it increases the amount of spin on approach shots taken with a club having a large loft angle, thus imparting the excellent control desired in particular by professionals and other skilled golfers.

In the golf ball of the present invention, the core may be made from a known core material which is prepared by blending, for example, a base rubber, the metal salt of an unsaturated carboxylic acid, and an organic peroxide.

The base rubber is preferably polybutadiene. The use of 1,4-polybutadiene, and especially one having a cis structure of at least 40%, is recommended. In addition to the polybutadiene, the base rubber may also include other rubbers such as natural rubber, polyisoprene rubber and styrene-butadiene rubber, if necessary.

Examples of suitable metal salts of unsaturated carboxylic acids include zinc dimethacrylate and zinc diacrylate. Zinc diacrylate is especially preferred for achieving a high rebound energy. It is advantageous to include such unsaturated carboxylic acids in an amount of at least 15 parts by weight, and preferably at least 20 parts by weight, but not more than 50 parts by weight, and preferably not more than 45 parts by weight, per 100 parts by weight of the base rubber.

Examples of suitable organic peroxides include 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, di-(t-butylperoxy)-m-diisopropylbenzene and 2,5-dimethyl-2,5-di-t-butylperoxyhexane. It is advantageous to include such peroxides in an amount of at least 0.1 part by weight, and preferably at least 0.5 part by weight, but not more than 5 parts by weight, and preferably not more than 2 parts by weight, per 100 parts by weight of the base rubber.

To impart good rebound characteristics, it is advisable to include a suitable compounding ingredient such as a thiophenol, thionaphthol, halogenated thiophenol or metal salt thereof in the core material. Specific examples of such compounding ingredients that may be used include pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol. The zinc salt of pentachlorothiophenol is especially preferred. Such a compounding ingredient is typically included in an amount of at least 0.4 part by weight, and preferably at least 0.6 part by weight, but not more than 2.0 parts by weight, and preferably not more than 1.2 parts by weight, per 100 parts by weight of the base rubber. Too much of this ingredient tends to lower the core hardness, which can adversely impact the feel of the ball when hit as well as its durability (cracking resistance), whereas too little may lower the rebound energy of the core, making it impossible for the ball to achieve a sufficient carry.

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If necessary, the core material may include also various additives such as inorganic fillers and antioxidants. Illustrative examples of such additives include zinc oxide, barium sulfate and calcium carbonate.

The core may be fabricated from the above core material by using a conventional process to blend the various ingredients and mold the resulting mixture. For example, the constituent ingredients may be blended in a suitable apparatus such as a Banbury mixer or a kneader to form a "slug," which is then placed in a mold where it is vulcanized at a temperature of generally at least 150° C., and preferably at least 160° C., but generally not more than 190° C., and preferably not more than 180° C. The period of vulcanization is generally at least 8 minutes, and preferably at least 12 minutes, but generally not more than 20 minutes, and preferably not more than 16 minutes.

The weight and diameter of the core may be suitably adjusted according to such factors as the constituent materials and thickness of the intermediate layer and the cover, which are described subsequently. It is recommended that the core generally have a weight of at least 23 g, and preferably at least 30 g, but not more than 37 g, and preferably not more than 35 g. It is also recommended that the core generally have a diameter of at least 33 mm, and preferably at least 36 mm, but not more than 39 mm, and preferably not more than 38 mm.

It is critical for the core to have an optimized hardness profile in which the hardness gradually increases radially outward from the center toward the outside edge or surface of the core. That is, the core has a higher hardness at the surface than at the center.

The core center and surface must have a difference between their respective measured JIS-C hardnesses of at least 18, preferably at least 20, and most preferably at least 22 units. This difference in hardness within the core gives the ball a low spin when hit with a driver (number 1 wood), enabling it to travel well and thus attain a good total distance. Too small a difference in JIS-C hardness between the relatively soft center and the relatively hard surface of the core allows the ball to take on too much spin when hit with a driver, so that it does not travel well and has a short run after it lands on the ground. This makes it impossible to achieve the desired distance. It is recommended that the upper limit in the hardness difference be at most 30, preferably 27 or less, and most preferably 25 units or less.

Specifically, the core at the center typically has a JIS-C hardness of at least 50, and preferably at least 55, but not more than 65, and preferably not more than 62. The core at the surface typically has a JIS-C hardness of at least 70, and preferably at least 75, but not more than 90, and preferably not more than 85. Too low a JIS-C hardness at the core center may deaden the feel and fail to achieve the desired rebound energy, whereas a hardness that is too high may result in an excessively hard feel when the ball is hit. Similarly, too low a JIS-C hardness at the core surface may deaden the feel of the ball when hit, while too high a hardness may result in too hard a feel.

Preferably the core of the inventive golf ball has a deformation of at least 3.0 mm, and preferably at least 3.3 mm, but not more than 5.0 mm, and preferably not more than 4.5 mm, when the load applied thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf). Too small a deformation may increase the spin when the ball is hit with a driver, preventing the desired travel from being achieved, and may also give the ball too hard a feel. On the other hand, too much deformation may deaden the feel and fail to achieve the necessary rebound energy.

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Since the core has a hardness gradually increasing radially outward from the center to the surface thereof and an optimized difference in hardness between the center and the surface where the core is hardest, the inventive golf ball having the above-described core functions to suppress the generation of excessive spin when it is hit with a driver, effectively increasing the run after it lands on the ground, and thus travelling a longer total distance.

The intermediate layer 3 of the inventive golf ball is an essential layer which is situated between the core 1 and the cover 2 of the ball G, as shown in FIG. 1, and is made of a resin material that is harder than the cover material. Even if the core and cover are within the scope of the present invention, a golf ball lacking the adequate intermediate layer prescribed by the present invention fails to attain the objects of the invention since it cannot adequately suppress spin when hit with a driver, making it impossible to achieve a longer travel distance, and gives a poor feel when hit.

The intermediate layer may be made using a known cover material, illustrative examples of which include an ionomer resin, either by itself or in admixture with a polyester, polyurethane, polyamide, polyolefin or polystyrene thermoplastic elastomer. The use of an ionomer resin by itself is especially preferred, although another thermoplastic resin may be used provided the resin material for the intermediate layer has a greater hardness than the cover. As with the cover material described below, pigments and various other additives may be included in the intermediate material.

The intermediate layer can be formed over the surface of the core using a known process, preferably an injection molding process. For example, once the core is placed within a mold, the intermediate layer material is injection molded over the core in a conventional manner.

The intermediate layer must have a greater hardness than the cover, which is described below. If the intermediate layer has a hardness which is the same as or lower than that of the cover, spin is not adequately suppressed when the ball is hit with a driver, in addition to which the ball has a lower rebound energy, preventing the anticipated total distance from being achieved. It is generally advantageous for the intermediate layer and the cover to have a Shore D hardness difference of at least 2, and preferably at least 5 units, but not more than 20, and preferably not more than 15 units.

It is recommended that the intermediate layer itself have a Shore D hardness of generally at least 50, and preferably at least 55, but not more than 67, and preferably not more than 65.

As already noted, the intermediate layer situated between the core and the cover in the golf ball of the invention has a greater hardness than the cover. The hardnesses of the intermediate layer and the core, when compared using the same hardness scale (i.e., JIS-C hardness or Shore D hardness), are preferably such that the intermediate layer has a greater hardness than the surface of the core. The JIS-C hardness difference between the intermediate layer and the core surface is preferably at least 2, and more preferably at least 6 units, but not more than 22, and more preferably not more than 18 units.

It is recommended that the intermediate layer have a thickness which is generally at least 0.5 mm, but not more than 3 mm, and especially not more than 2 mm. In cases where there are two or more intermediate layers, it is advisable to set the overall thickness of the intermediate layers within the above range.

If the golf ball has two or more intermediate layers situated between the core and the cover, the above-described

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hardness relationship must be maintained between the cover and the outer intermediate layer which is in close contact with the cover.

The cover of the golf ball is formed of a material which is softer than the intermediate layer material. Examples of suitable cover materials include ionomer resins and polyurethane thermoplastic elastomers which are softer than the intermediate layer material. The use of an ionomer resin is especially preferred.

It is advantageous for the cover to have a Shore D hardness of generally at least 45, and especially at least 48, but not more than 60, and especially not more than 58. A hardness value that is too low may result in increased spin and an inability to achieve the required total distance. On the other hand, a hardness value that is too high may adversely impact the controllability of shots taken with an iron club having a large loft angle, and approach shots.

A conventional process may be used to form the cover. It is especially preferable to use an injection molding process in which a solid core over which an intermediate layer has been formed is placed within a mold, and the cover material is injection molded over the intermediate layer.

It is recommended that the cover generally have a thickness of at least 0.6 mm, and preferably at least 1.0 mm, but not more than 2.1 mm, and preferably not more than 1.8 mm. Too thin a cover may lower the durability of the ball, whereas a cover that is too thick may lower the ball's rebound energy.

Since the golf ball of the invention has an optimized balance in hardness among the various layers as described above, the ball is endowed with an excellent rebound energy, distance performance, feel, controllability and spin characteristics.

For competition play, the golf ball of the invention may be formed so as to have a diameter and weight which conform with the Rules of Golf. That is, the ball may have a diameter of not less than 42.67 mm and a weight of not greater than 45.93 g.

EXAMPLES

Examples of the invention and comparative examples are given below by way of illustration, and are not intended to limit the invention.

Examples 1-3 and Comparative Examples 1-5

To ascertain the flight characteristics and feel of golf balls according to one embodiment of the invention, golf balls

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with different hardnesses at the center and surface of the core were produced in Examples 1, 2 and 3. A number of additional examples were carried out for the purpose of comparison. The golf balls produced in Comparative Example 1 had cores with a small or flat hardness profile. The balls produced in Comparative Example 2 had cores with a noticeable, yet gradual, hardness profile. The balls produced in Comparative Example 3 had a core with a distinct hardness profile, but had an intermediate layer that was softer than the cover. The balls produced in Comparative Examples 4 and 5 similarly had cores with distinct hardness profiles, but lacked an intermediate layer. Comparative tests were conducted on these various balls.

The balls were all given the same arrangement of dimples on the surface of the cover. Namely, each ball had a total of 432 dimples of three types formed on the cover in an icosahedral arrangement.

Tables 1 and 2 below show the characteristics of the cover and intermediate layer in the ball samples in each example. Table 3 gives the characteristics of the core in the same balls, and Table 4 presents the test results obtained for each type of ball.

TABLE 1

	Cover	Example			Comparative Example				
		1	2	3	1	2	3	4	5
Inter- mediate layer	Material	a	a	a	a	a	b	a	a
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
	Hardness (Shore D)	55	55	55	55	55	65	55	55
Cover	Material	b	b	b	b	b	a	—	—
	Thickness (mm)	1.5	1.5	1.5	1.5	1.5	1.5	—	—
	Hardness (Shore D)	65	65	65	65	65	55	—	—

TABLE 2

	Cover, intermediate layer	a	b
Composition (parts by weight)	Himalan AM7317 (Zn) ¹⁾ Himalin 1650 (Zn) ²⁾ Himalin AM7318 (Na) ³⁾ Surlyn 8120 (Na) ⁴⁾	50	50
Hardness	Titanium oxide Shore D hardness JIS-C hardness	5 55 80	5 65 94

¹⁾A zinc ionomer resin having an acid content of 18% made by DuPont-Mitsui Polymers Co., Ltd.

²⁾A zinc ionomer resin made by DuPont-Mitsui Polymers Co., Ltd.

³⁾A sodium ionomer resin having an acid content of 18% made by D.R. & M. Inc., Indianapolis, Ind.

DuPont-Mitsui Polychemicals Co., Ltd.
A sodium ionomer resin made by E. I. DuPont de Nemours and Co.

¹A sodium ionomer resin made by E. I. DuPont de Nemours and Co.

TABLE 3

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TABLE 3-continued

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Vulcan-	Zinc salt of pentachlorothiophenol	1	1	1	0.2	0.2	1	1	1
ization	Primary Temperature (° C.)	175	175	175	140	155	175	175	175
conditions	Time (min)	15	15	15	30	15	15	15	15
	Secondary Temperature (° C.)	—	—	—	165	—	—	—	—
	Time (min)	—	—	—	15	—	—	—	—
Hardness	Surface (JIS-C hardness)	85	83	78	76	76	83	87	80
	Center (JIS-C hardness)	61	59	55	72	60	59	63	56
	JIS-C hardness difference	24	24	23	4	16	24	24	24
	Deformation under loading (mm) ⁵	3.4	3.8	4.1	3.3	3.4	3.8	3.4	4.1

¹Dicumyl peroxide, produced by NOF Corporation under the trade name Percumyl D.²1,1-Bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, produced by NOF Corporation under the trade name Perhexa 3M-40.³Zinc white-containing sulfur, produced by Tsurumi Chemical Industry Co., Ltd.⁴Nocrack NS-6, produced by Ouchi Shinko Chemical Industrial Co., Ltd.⁵Deformation under loading from an initial load of 98 N to a final load of 1,275 N.

TABLE 4

		Example			Comparative Example				
		1	2	3	1	2	3	4	5
Flight ¹	Carry (m)	233.0	232.2	231.1	233.2	232.1	232.5	231.8	229.5
	Total distance (m)	241.2	243.8	244.9	238.5	239.9	245.3	238.3	241.1
	Spin (rpm)	2805	2745	2700	2910	2855	2550	2952	2847
	Rating	good	good	good	poor	poor	good	poor	fair
Approach ²	Spin (rpm)	5833	5821	5811	5849	5830	4100	5870	5832
	Rating	good	good	good	good	good	poor	good	good
Feel ³	When hit with driver	good	good	good	good	good	good	good	poor
	When hit with putter	good	good	good	good	good	poor	good	good

¹Flight was rated as follows, based on distance measured when ball was hit at a head speed of 50 m/s by a driver mounted on a swing robot.

Good: Total distance at least 241 m.

Fair: Total distance at least 241 m, but carry less than 230 m.

Poor: Total distance 240 m or less.

²Approach was rated as follows, based on spin rate measured when ball was hit at a head speed of 19 m/s by a sand wedge mounted on a swing robot.

Good: Good spin (at least 5,500 rpm).

Poor: Inadequate spin (less than 4,500 rpm).

³Average sensory evaluations for five professional golfers:

Good: Feel was appropriate and good.

Poor: Feel was too hard or too soft.

As is apparent from the results in Table 4, the golf balls according to the invention all showed a good balance of distance, controllability on approach shots, and feel.

By contrast, the golf balls produced in the comparative examples each had drawbacks. In Comparative Examples 1 and 2, the hardness difference between the surface and center of the core was less than 18, resulting in much spin and a poor distance when the ball was hit with a driver. In Comparative Example 3, the cover was harder than the intermediate layer, and had an excessively high hardness. As a result, the amount of spin on approach shots was low and controllability was poor. In addition, the feel when hit with a putter was poor. The golf balls produced in Comparative Example 4 were two-piece balls which lacked between the cover and the core an intermediate layer of greater hardness than the cover. These balls had a lot of spin when hit with a driver, and thus a poor distance. In the golf balls produced in Comparative Example 5, the core hardness was lowered to reduce the high spin rate on impact with a driver in Comparative Example 4, but the resulting feel on impact with a driver was too soft.

Japanese Patent Application No. 2000-190640 is incorporated herein by reference.

Although some preferred embodiments have been described, many modifications and variations may be made thereto in light of the above teachings. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without departing from the scope of the appended claims.

What is claimed is:

1. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and said elastic core has a hardness which gradually increases radially outward from the center to the surface thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

2. The golf ball of claim 1, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90.

3. The golf ball of claim 1, wherein said core undergoes a deformation of 3.0 to 5.0 mm when the load applied

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thereto is increased from an initial load of 98 N (10 kgf) to a final load of 1,275 N (130 kgf).

4. The golf ball of claim 1, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units.

5. The golf ball of claim 1, wherein the intermediate layer has a Shore D hardness of 50 to 67.

6. The golf ball of claim 1, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units.

7. The golf ball of claim 1, wherein the cover has a Shore D hardness of 45 to 60.

8. The golf ball of claim 1, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover.

9. The golf ball of claim 1, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

10. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

11. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol.

12. The golf ball of claim 1, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

13. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover, and has a greater hardness than the surface of the elastic core when compared using the same JIS-C hardness scale, and said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

14. The golf ball of claim 13, wherein said core at the center has a JIS-C hardness of 50 to 65, and at the surface a JIS-C hardness of 70 to 90.

15. The golf ball of claim 13, wherein the difference in JIS-C hardness between the center of the elastic core and the surface thereof is 22 to 30 units.

16. The golf ball of claim 13, wherein the intermediate layer has a Shore D hardness of 50 to 67.

17. The golf ball of claim 12, wherein the JIS-C hardness difference between said intermediate layer and said core surface is 2 to 22 units.

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18. The golf ball of claim 12, wherein the cover has a Shore D hardness of 45 to 60.

19. The golf ball of claim 12, wherein the golf ball has two or more intermediate layers situated between the core and the cover, and said hardness relationship is maintained between the cover and the outer intermediate layer which is in close contact with the cover.

20. The golf ball of claim 12, wherein the core is formed of rubber as a base and the cover is formed of materials including ionomer resins and polyurethane thermoplastic elastomers.

21. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

22. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentafluorothiophenol.

23. The golf ball of claim 13, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

24. A golf ball comprising a rubbery elastic core having a center and a radially outer surface, a cover having a plurality of dimples on the surface thereof, and at least one intermediate layer situated between the core and the cover; wherein

said intermediate layer is composed of a resin material which is harder than the cover having a Shore D hardness of 45 to 58 and has a greater hardness than the surface of the elastic core when compared using the same hardness scale, and

said elastic core has a hardness at the center and a hardness at the surface thereof which is greater than the hardness at the center thereof, and a difference in JIS-C hardness of at least 22 between the center and the surface.

25. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of thiophenol, thionaphthol, halogenated thiophenol and metal salt thereof.

26. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient selected from a group consisting of pentachlorothiophenol, pentafluorothiophenol, pentabromothiophenol, p-chlorothiophenol and the zinc salt of pentachlorothiophenol.

27. The golf ball of claim 24, wherein said elastic core is formed of rubber as the base material comprising an ingredient of zinc salt of pentachlorothiophenol added in an amount of 0.4 to 2.0 parts by weight, to per 100 parts by weight of the base rubber.

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EXHIBIT 12

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT 13

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT 14

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**

EXHIBIT 15

**THIS EXHIBIT HAS BEEN
REDACTED IN ITS ENTIRETY**